EQUILIBRIUM BETWEEN FERROUS AND FERRIC IRON WHEN SUBJECTED TO AN ALTERNATING CURRENT

A THESES SUBMITTED TO THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF ARTS.

BY

JAMES GORDON ROBINSON, A. B. COOPER COLLEGE

1915

When in solution, iron may be found in the ferric (Fe^{+++}) or ferrous (Fe^{++}) state. The relative proportions of ferric and ferrous iron in any solution depend upon the extent to which the ions in the solution have been electrically charged. If all the ions have received charges corresponding to the limit (three positive charges) or all ions are Fe^{+++}, then the solution contains nothing but ferric iron. Some of the ions may have lost one positive charge, causing the solution to contain a mixture of ferric and ferrous iron. If the number of positive charges per ion have been reduced to the lower limit (two) the solution contains nothing but ferrous iron.

It is then evident that the character of an iron solution is largely dependent upon the number of positive charges carried by its ions. Also if a change can be made in the number of positive charges, the constitution of the solution may be changed from 100% ferric and no ferrous to no ferric and 100% ferrous at will.

It has been shown by Allen[1] that with suitable electrodes and electric current, generated within the solution, or from an outside source; a solution of iron 100% ferric may be quickly changed to 100% ferrous and no ferric. If positive charges can be removed from the ions by suitable means it is reasonable to suppose that a reversal of conditions might be brought about in which these positive charges might be again placed upon the ions changing a ferrous solution back to ferric. Also if the solution were subjected to an alternating current the ions would alternately gain and lose positive charges.

As is commonly known the direct electric current produced by

1 J. Chem. Soc. 36.492 (1914)

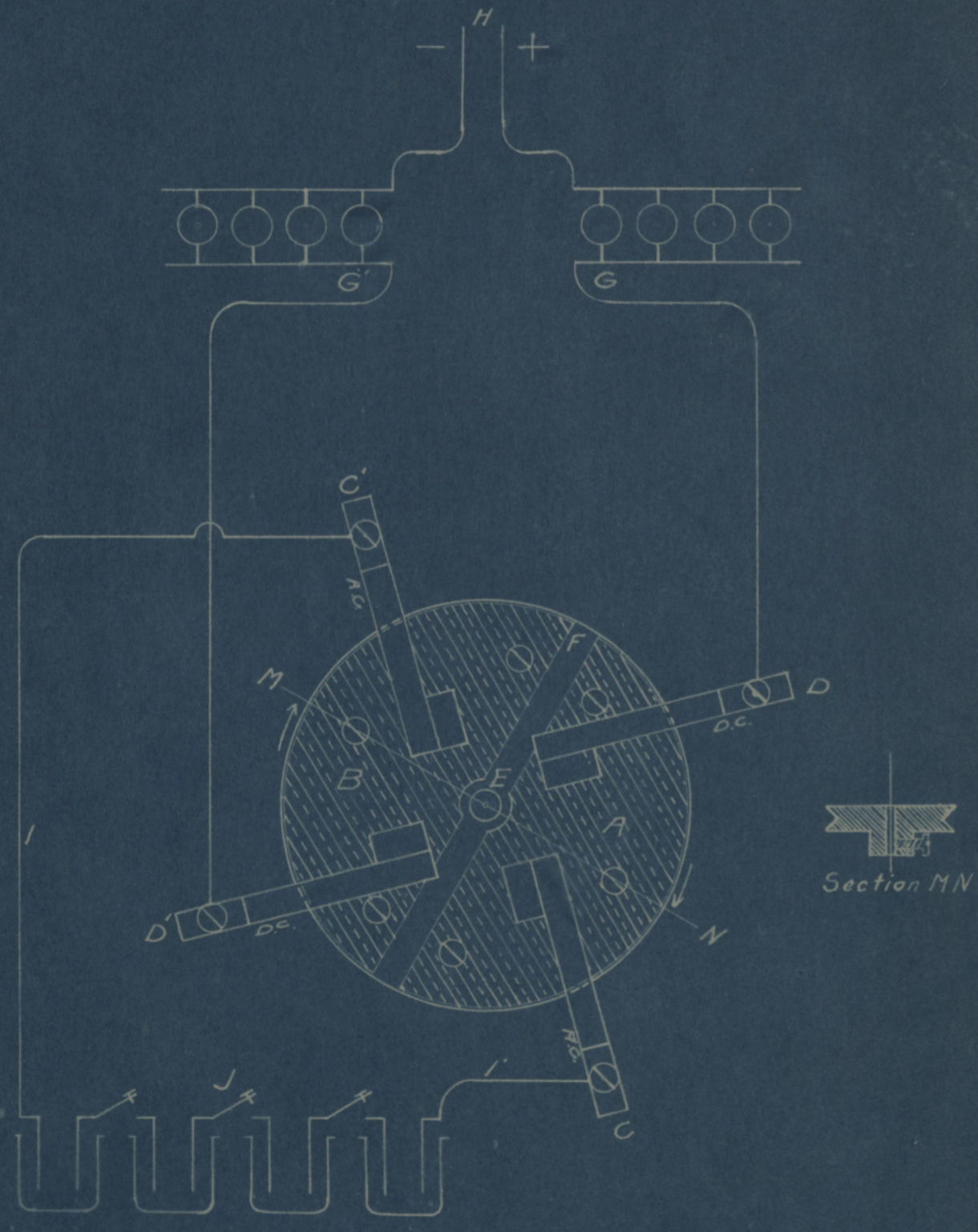
a dynamo consists of a large number of impulses overlapping one another and producing a current of practically uniform voltage and amperage. This is not altogether true of the alternating current for in this case there is a flow of electricity first in one direction and then in the other. The curve representing y=sin x very nearly represents the rise and fall of the voltage. So the current is sometimes called a sin wave current. The number of reversals, or alternations per second may vary from twenty-five and sixty of the commercial power and light circuits to two thousand or more of the special high frequency generators. Lower frequencies than twenty-five cycles per second must be obtained by commutator devices of one kind or another.

The action of the direct current upon ferric ions having been established it is desired to know the results when using an alternating current under varying conditions of temperature, frequency, etc.

Apparatus. The apparatus requirments include a revolving electrode machine. In the earlier work one having six revolving electrodes and the usual accessories of lamp and sliding resistances etc., was used. For the latter part a smaller, four electrode machine was used, similar to the above except that the revolving electrodes were adjustable in a perpendicular direction. This latter feature made it possible to raise or lower the electrodes. The speed of rotation ranged from 600 to 700 revolutions per minute. In the latter part of the investigation the speed ranged between 675 and 700.

The only alternating currents available being a sixty cycle current for lighting purposes and that produced by a Siemens, Schuckert high frequency motor generator, it was decided to prepare a commutator

PLATE. 1.



Variable Frequency Apparatus.

apparatus for the lower frequencies and to use the Siemems, Schuckert motor-generator for frequencies of 750 to 2000 per sec. The construction of the apparatus for the low frequencies was as follows: Upon the lower end of one of the revolving electrodes of the apparatus was mounted a disc of wood (See Plate 1.) which had been boiled in paraffin. The disc was three and one-half in. in diameter. Upon its upper face were fastened with screws two half circles of brass A, B. For better insulation, two layers of sheet mica were placed upon the wood beneath the brass. Bearing upon the brass half-circles were four copper brushes spaced 90° apart. From a source of direct current of 110 volts at H, the brushes D and D' were supplied. The current was led off through the solution from, 1, 1'. When the disc carrying the brass half circles was rotated there were four reversals of current per revolution, or two cycles in the circuit 1, 1'. With the most careful setting of the brushes there was a greater flow of current in one direction than in the other, through 1, 1'. This was overcome by making one run, or determination, then interchanging the connection at H, and making a second run. The results were then averaged. Considerable sparking occured at the brushes on account of the 110 volt direct current. To over come this a lamp resistance G, G' was introduced into the supply circuit. To preserve a balance the number of lamps in use at any time in G was kept equal to that in G'.

For heating the solution to temperatures higher than room temperature two methods were available. First, by heat from a gas-burner or electric hot-plate, or second, by passing a large current through the solution. By using a low outside resistance a temperature as high as 65° could be reached. No more current could be passed through without interruption at the smaller electrode. Owing to this difficulty

and to the fact that it might be desirable to study the effect of small current strengths and still maintain the higher temperatures this method was soon discarded in favor of the hot-plate. With moderate attention, the solution in the beaker upon the plate could be kept at temperatures ranging up to 95°. During any run, the range is usually 5° and never more than 10°. For temperature lower than 35°, a mixture of salt and ice is used.

All burets used were either Government standardized or common ones standardized by weight. To contain the solution and electrode, 300 cc plain beakers were used. 225 cc in a beaker of this size covered the electrodes to the depth of three cm. The electrodes were all of platimum wire, disc or gauze. The discs were 3 cm in diameter attached at the center at right angles to a #12 wire 10 cm in length. By rolling, the gauze was formed into a spiral, fastened at the inner end to the support, with the outer end free to hook around the solution (See note 1). The wire electrode was exposed for 20 mm of its length the remainder being covered with glass.

Chemicals: All chemicals used were c.p. Ferrous sulfate being easily oxidized when in contact with the oxygen of the air, it was kept covered in the stock bottle and in the buret by oxygen free natural gas. In an interval of eight days the variation in the ratio between the potassium permanganate, kept in colored glass, and the ferrous sulfate did not exceed .53%.

As before stated the ways in which the problem might be studied are varied but the present investigation will be limited to the following and will be discussed in the order named; preliminary, including oxidation by the air while stirring, acid concentration, temperature, and frequency of alternations.

1. J. Chem. Soc. 36, 938 (1914) Allen.

Procedure. The ferrous and ferric solutions were measured into the beaker from the burets. The acid was then added and the whole solution was made up to 225 cc with water. The beaker was then placed upon the machine and the electrodes adjusted to positions beneath the surface. The machine was then started and kept in motion for the chosen length of time. After the run was completed the solution was titrated with the potassium permanganate. The amount of oxidation or reduction that had taken place during the run was indicated by the amount of permanganate used.

Experimental Part.

In order to determine the amount of oxidation due to the action of the air in the open beaker, the following trials were made: Table 1.

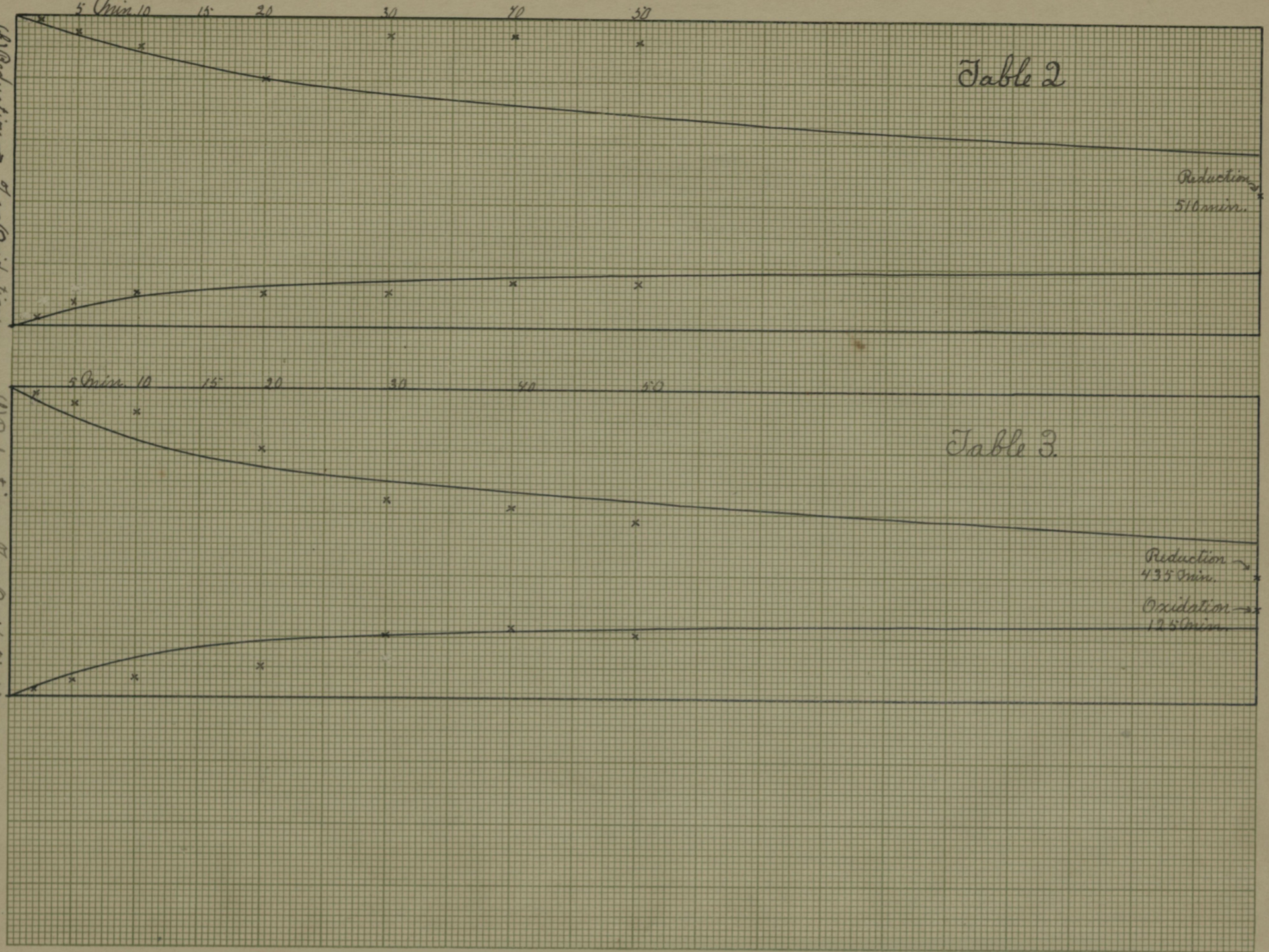
Revolving electrode: Pt gauze 7979.6 sq. mm. Stationary electrode: Pt wire 12.6 sq. mm. Total volume of solution 225 cc. Proportion of iron expressed as % Fe^{+++} the remaining % being Fe^{++}. Time of run: 20 min.

Trial	Temperature	%Fe^{+++} at start	% oxidation
1	90.0°	0.14	1.00
2	90.3°	48.35	.11

During all the trials, including the above, all percautions such as submerging the revolving electrode, keeping it near the side of the beaker to avoid vortex action, etc. were observed. The trials of Table 1 gives data for the correction of later observation.

The process of oxidation, wherever it occurs, involves a change in the number of charges upon some ion. In the solution under consideration the change is, in part, represented by the following equation:[1] $4\,Fe^{++} + O_2 + 2\,H_2O = 4Fe^{+++} + 4\,OH^-$. This equation shows

1. Oswald p. 577 (1904 Ed.)



clearly the change in charge, (one positive added,) on the ferrous ion but does not show from whence the additional positive charge came. Evidently it did come from the O_2, and in order to state positively the source of this additional positive quantity of electriaity we must inquire further into the structure of the oxygen molecule, O_2. Practically all of the oxygen of the air is combined as O_2 and the surface of the liquid in the beaker being uncovered oxidation might be assumed to be taking place, in the surface layers all of the time. The above data made possible correction for the oxidation of different concentrationsof ferrous iron.

To show as clearly as possible the results from the acidity, temperature, and frequency trials, all succeeding data is tabulated and plotted upon coordinate paper. Whenever advisable smooth curves are drawn. Unless indicated other wise, all the conditions are the same as those of the trial just preceding. Where parallel trials are made, one starting with 100% $Fe^{+++}$and no Fe^{++} and the other 100% Fe^{++} and no Fe^{+++} , the results are shown in the tables and indicated as (a) and (b) as also upon the coordinate paper.

Table 2. (a) Oxidation (by current only).

Room temperature at start. Acidity: Unchanged from original solution. Ferrous solution: $Fe(NH_4)_2(SO_4)_2$. Total volume of solution: 175 cc. 100% Fe^{++} .

Trial	Current (Amp.)	Time (Min)	$KMnO_4$ cc	cc oxidized.	% oxidation
1	0	0	14.72	0	0
2	3.75	2	14.29	.43	2.92
3	3.75	5	13.65	1.07	7.27
4	3.75	10	13.10	1.62	11.01
5	3.75	*20	13.14	1.58	10.74
6	1.5	30	13.01	1.71	11.62

Table 2(a) continued.

7	1.5	40	12.63	2.09	14.19
8	1.5	50	12.63	2.09	14.19

*Because of the large current the temperature rose to nearly 100° at the end. Reference to the table and to the corresponding graph under "Table 2" will show the comparatively rapid oxidation at the beginning up to ten minutes. After this the oxidation comes nearly to a standstill and the curve representing the oxidation flattens out nearly to the horizontal. On account of the high temperature resulting from the large current (3.75 amp) it was reduced to 1.5 amp. This caused a falling off, as might be expected for the 30, 40, and 50 minute runs.

Table 2 (b) Reduction.

Iron solution: $Fe_2(SO_4)_3$ Vol. of Fe sol. 50 cc made up to 175cc. 100 % Fe^{++} at start.

Trial	Current	Beginning and end temp.	Time.	KMNO4 used	cc reduced	% reduction.
1	0	30°	0	.18	0	0
2	3.75	30-34	2	.58	.40	1.59
3	3.75	31-40.5	5	1.39	1.21	4.82
4	3.75	31-47.5	10	2.65	2.47	9.84
5	3.75	31-60	20	5.06	4.88	19.44
6	1.5	31-39.5	30	1.49	1.30	5.22
7	1.5	32.5-41.5	40	1.41	1.23	4.89
8	1.5	32.5-42.5	50	2.15	1.87	7.44
9	1.5	-	510	13.10	12.92	51.45

The change here is quite rapid but is a reduction and not an oxidation as in Table 2(a). More noticable however is the apparent tendency toward an equilibrium some where below 50% Fe^{+++} but since these runs were made in order to determine the effect of the acid pre-

sent we will call attention to the amounts of oxidation Table 2(a) at 20 min. 10.74%, and the reduction, Table 2(b) at 20 min. 19.44% and 51.45% at 510 min. The sudden change at 30 min. where the current was reduced to 1.5 amp, may of course be due to the decreased opportunity for the exchange of electric charges but in the light of later work seems more likely due to the lower temperature maintained by the solution.

A further reduction in current was made in the following runs. The temperature was kept above 30° by applying heat:

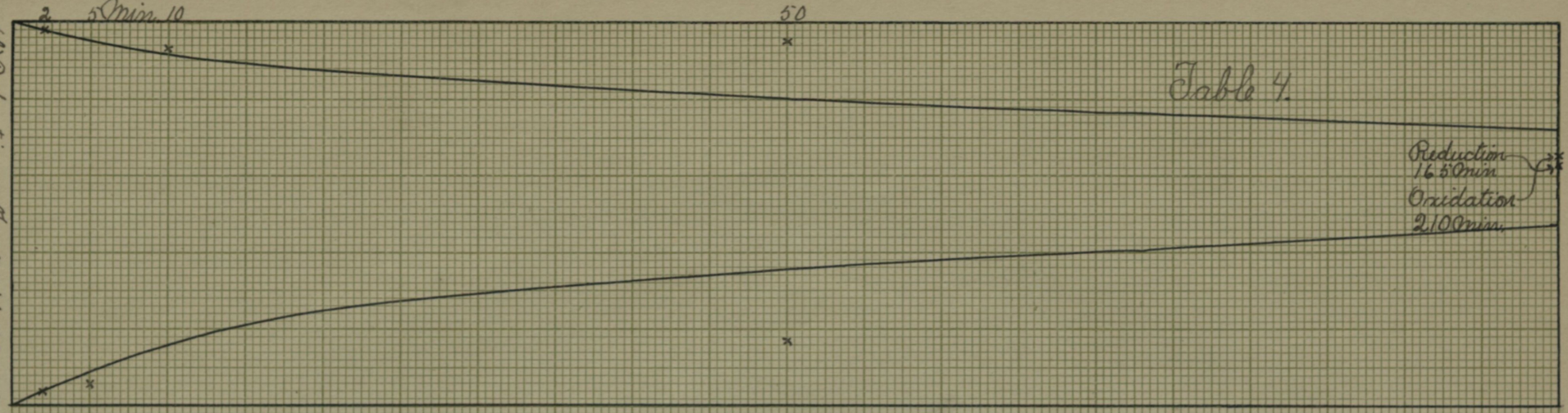
Table 3(a) Oxidation.

Current .75 amp.

Trial	Temp.	Time	$KMnO_4$	cc oxidized	% oxidation
1	-	0	25.58	0	0
2	60-70	2	24.92	.66	2.58
3	68-76	5	24.18	1.40	5.44
4	70-80	10	23.97	1.61	6.30
5	60-81	20	22.82	2.76	10.80
6	52-80	30	20.32	5.26	20.57
7	56-79	40	19.50	6.08	23.82
8	61-79	50	20.09	5.49	21.48
9	34-70	125	17.66	7.92	30.95

Table 3(b) Reduction.

Trial	Temp	Time	$KMnO_4$	cc reduced	% reduction
1	70	0	.13	0	0
2	70	2	.58	.45	1.80
3	71-68	5	1.21	1.08	4.28
4	71-68	10	2.00	1.87	7.42
5	71-74	20	5.06	4.93	19.54
6	70-70	30	9.10	8:97	35.54
7	70-71	40	9.73	9.60	38.02



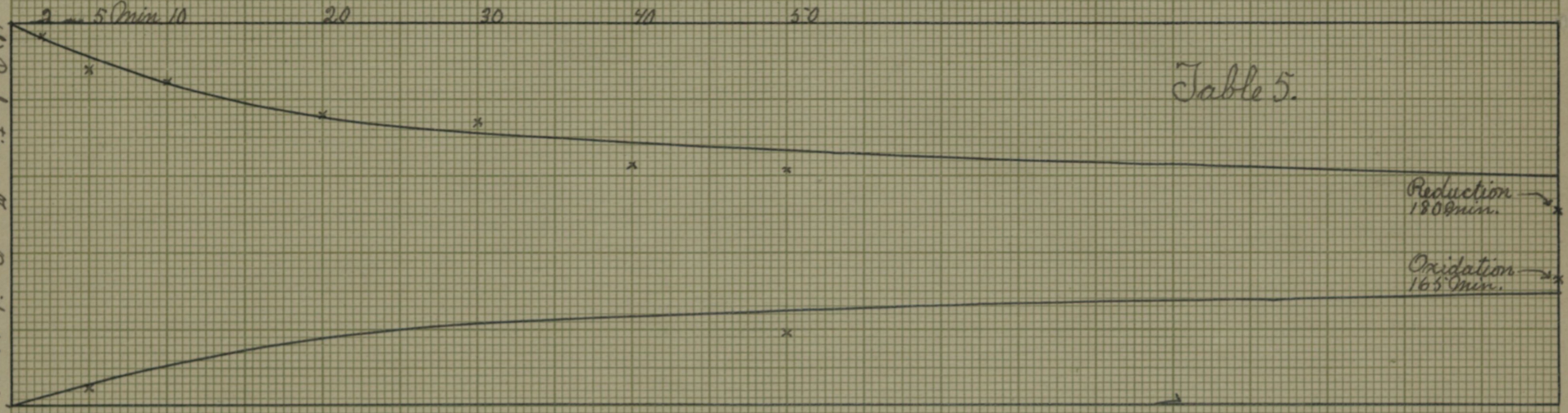


Table 3(b) continued.

8	70-71	50	10.73	10.60	42.10
9	70-71	435	14.84	14.71	58.35

The tendency toward equilibrium below 50% Fe^{+++} continues, while oxidation (in (a)) and reduction (in (b)) continue regularly at the higher temperatures even though the current has now become .75 amp. At 20 min. the oxidation was 10.80%, and the reduction at that time 19.54%. At 125 min. the oxidation was 30. 95% and the reduction at 435 min, was 58.35%.

35 cc of conc. $H_2 SO_4$ (sp. gr. 1.84) were now added and the temperature kept at 70°

Table 4.(a) Oxidation.

Trial	Time	cc oxidized.	% oxidized
1	2	1.10	4.34
2	5	1.56	6.16
3	50	4.26	16.78
4	210	16.51	65.02

Table 4 (b) Reduction.

Trial	Time	cc oxidized	% oxidized
1	2	.49	1.95
2	10	1.58	6.29
3	50	1.15	4.58
4	165	9.37	37.10

At the end of 5 min. the oxidation was 6.16% at the end of 210 min. 65.02 %. The reduction at the end of 10 min. 6.29% and at the end of 165 min. 37.10%. The addition of the acid evidently has had its effect upon both oxidation and reduction producing a tendency toward equilibrium somewhere above 50% Fe^{+++} thereby suggesting the possibility of varying

the oxidation and reduction at will by such addition. As a desirable method it cannot however commend itself on account of the extreme slowness, anywhere from one to three hours being required to bring the oxidation and reduction per cents together.

The effect of the added $H_2 SO_4$ again appears in the following set of runs where the amount added is reduced from the 35 cc of the table just given to 10 cc. Let it also be noticed that the current strength is raised.

Table 5(a) Oxiation

10 cc $H_2 SO_4$ added. Current: 2.5 amp.

Trial	Time	cc oxidized	% oxidized
1	5	1.44	5.7
2	50	4.89	19.4
3	165	8.34	33.1

Table 5 (b) Reduction.

Trial	Time	cc reduced	% reduced
1	2	.70	2.79
2	5	2.84	11.3
3	10	3.62	14.4
4	20	5.89	23.4
5	30	6.45	25.6
6	40	9.14	36.4
7	50	12.05	48.0
8	180	12.53	49.7

As might be expected the paths of both oxidation and reduction curves lie intermediate to those of Tables 3 and 4. At 50 min. the oxidation of Table 5 is 19.4%, of Table 3, the one with the least acid, 21.48% and of Table 4, 16.78%. The results in reduction are even better being

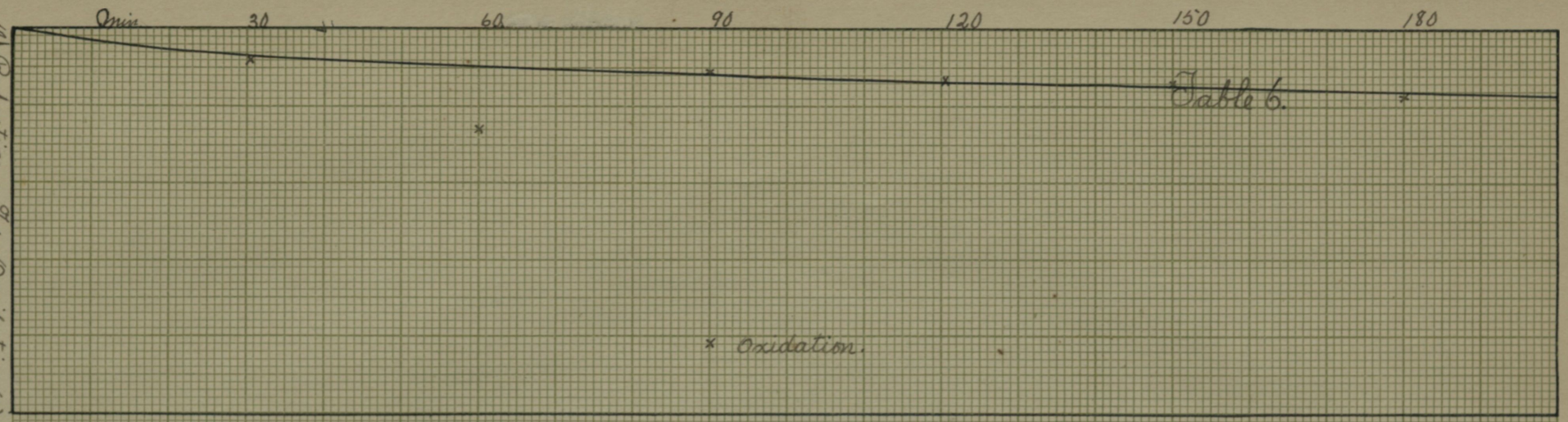


Table 6.

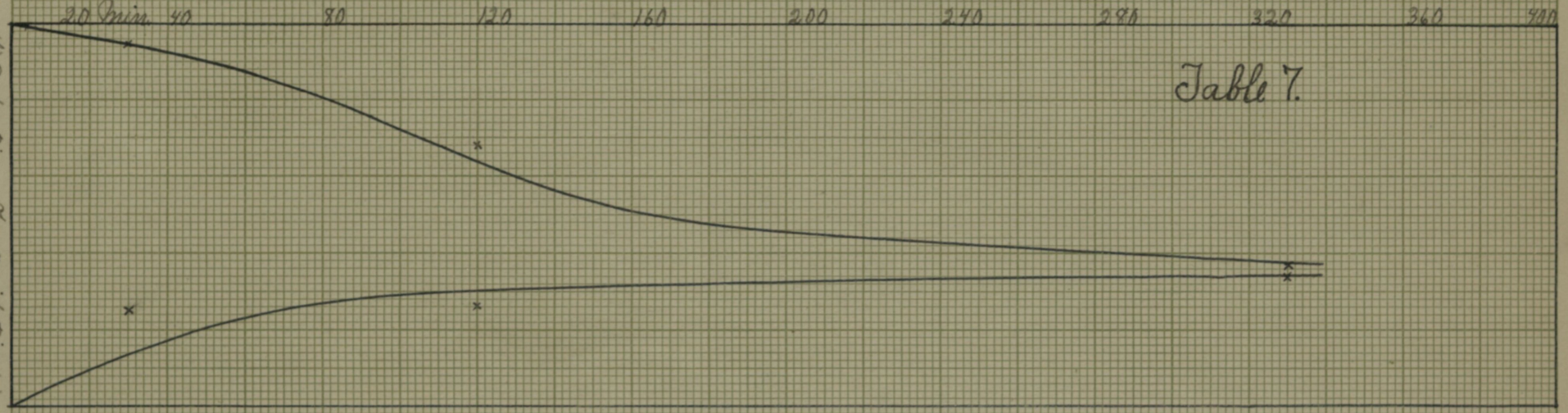


Table 7.

at 50 min. in Table 5., 48.0% in Table 3, 42.10% and in Table 4, 4.58%. Equilibrium appears again to be established a little below 50%.

A great deal of time is required in making the longer runs and where a limited number of rotating electrodes are available this is inconvenient. To save time the amount of solution was increased, disc electrodes, placed well down into the solution, were substituted for the gauze and small portions removed by means of a pipet at short intervals for titrtion.

Table 6 (a) Oxidation.

10 cc removed for titration at 30 min. intervals. Total volume increased to 250 cc. Fe and $H_2 SO_4$ increased in proportion.

Interval	cc oxidized	% oxidation
3(90 min.)	.53	16.4

Table 6 (b) Reduction.

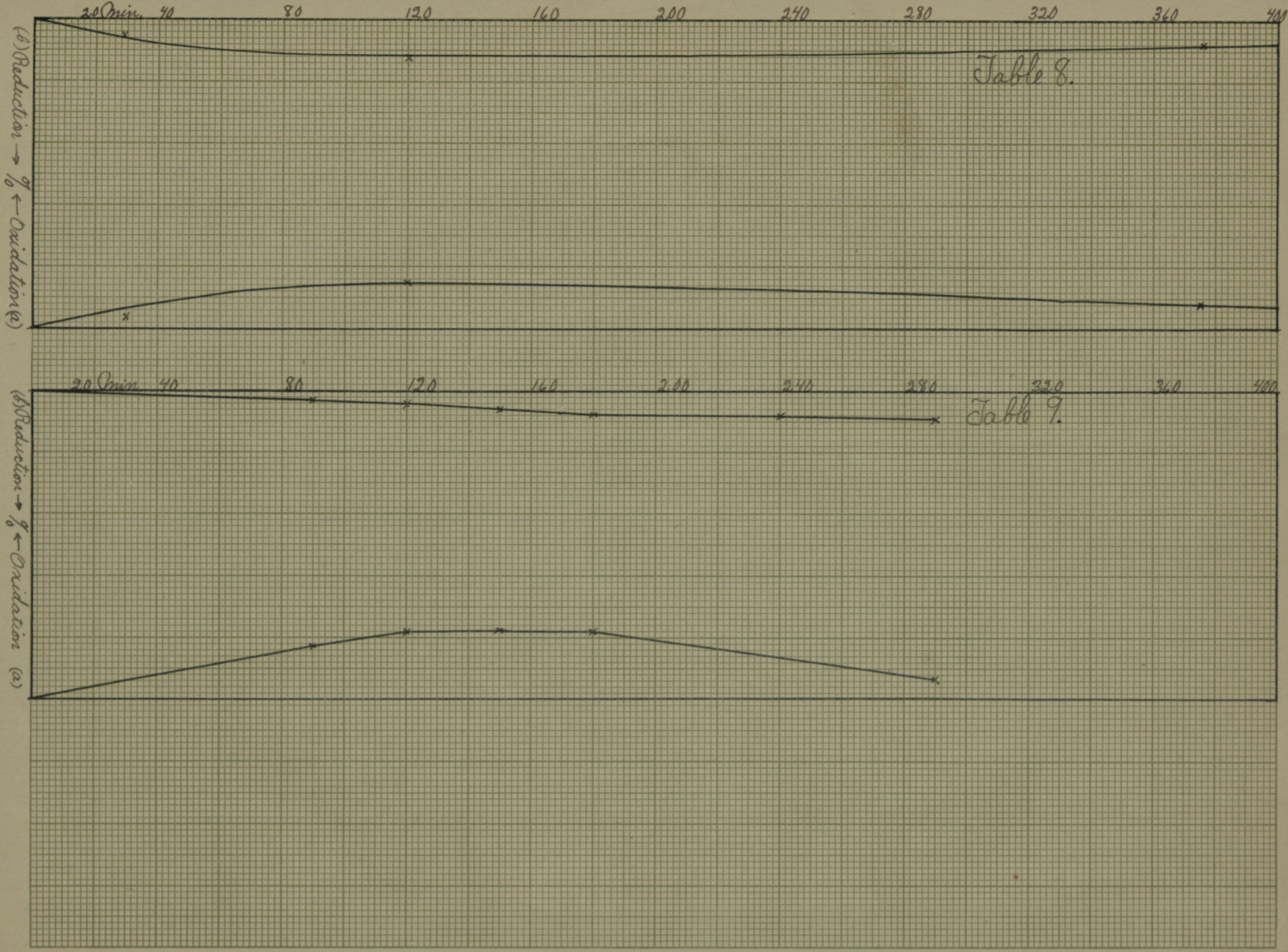
Interval	cc reduced	% reduction
1 (31 min.)	.26	8.1
2	.885	26.5*
3	.39	12.1
4 (121 min.)	.44	13.6
5 (150 min.)	.50	15.5
6	.59	18.0

* Unusual reduction. Perhaps due to a mass of reduced solution taken up by the pipet.

The small surface of the disc electrodes makes the action very slow. The results are similar to those represented by Table 3. To increase the accuracy in titration a larger portion was taken out with the pipet and to quicken the reaction the temperature was raised as shown by:

Table 7 (a) Oxidation.

25 cc pipetted and titrated. Temp.42°. Current 1 amp.



Time	cc oxidized	% oxidized
30	1.97	24.3
120	2.07	25.5
330	2.69	33.2

Table 7 (b) Reduction.

Time	cc reduced	%
30	.42	5.2
120	2.23	32.7
330	5.06	63.0

The oxidations and reductions are both more rapid. Equilibrium is established below 50%.

The acidity was again raised to 35 cc $H_2 SO_4$ to 175 cc of the solution.

Table 8 (a) Oxidation.

35 cc $H_2 SO_4$ to 175 cc sol. (Total vol. 250 cc.)

Time	Temp	cc oxidized	%
30	43.5	.32	3.95
120	42.0	1.17	14.4
375	43.0	.60	7.4

Table 8 (b) Reduction.

Time	Temp	cc reduced	%
30	43.0	.46	5.7
120	41.5	1.04	12.9
375	44.0	.69	8.1

Oxidation and reduction both fall off after 12° min.

It was suggested that the introduction of the NH_4 along with the Fe of the $(NH_4)_2 Fe (SO_4)_2$ by forming other compounds was responsible for the falling off mentioned above. A solution of reduced

$Fe_2(SO_4)_3$ was substituted for the ferrous ammonium sulphate.

Table 9

For the Fe^{++} solution, was used a solution of $Fe_2(SO_4)_3$ reduced with copper gauze cathode and amalgamated zinc anode! Revolving electrode:

Pt disc 35 mm diameter. Total submerged area 2299 sq. mm. 60 cc H_2SO_4 to 175 cc of solution.

(a) Oxidation.

Time	Temp	cc titrated	cc oxidized	%
90	43.0	10	.625	17.2
120	43.0	10	.79	21.7
150	44.0	10	.805	22.1
180	44.0	10	.805	22.1
290	-	25	1.52	16.7

(b) Reduction

Time	Temp	cc titrated	cc reduced	%
90	44.0	10	.085	2.3
120	44.0	10	.15	4.1
150	-	10	.225	6.2
180	44.0	10	.28	7.7
240	44.0	10	.305	8.2
290	-	25	.795	8.7

The falling off may still be seen in the oxidation, in which reduced $Fe_2(SO_4)_3$ was used. It does not show in the reduction. It is therefore probable that this falling off is due to imperfect stirring or other experimental cause. Certainly not to the formation of NH_4 compounds. It must also be pointed out that the oxidation has been increased by the addition of the large amount of acid and the reduction decreased which is in accord with the results in Tables 4 and 7 with

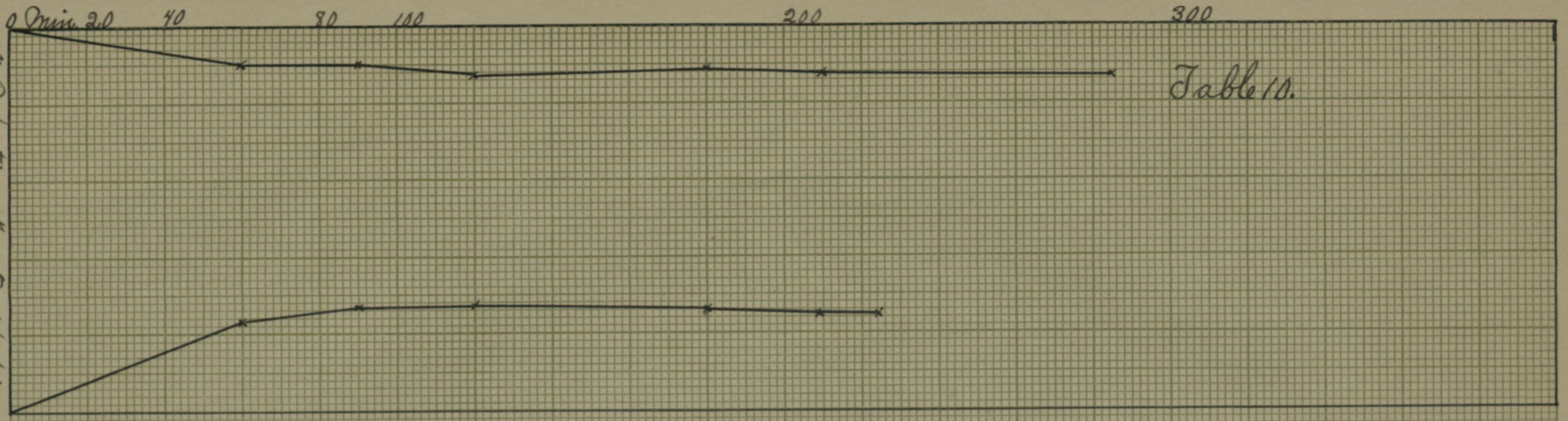


Table 10.

Table 11.

acidity 35 cc to 175 cc of solution.

The acid was reduced to 35 cc to 175 cc in the following:

Table 10

35 cc H_2SO_4 to 175 cc of solution. Temp: 35°-36°. 10 cc pipetted and titrated.

(a) Oxidation.

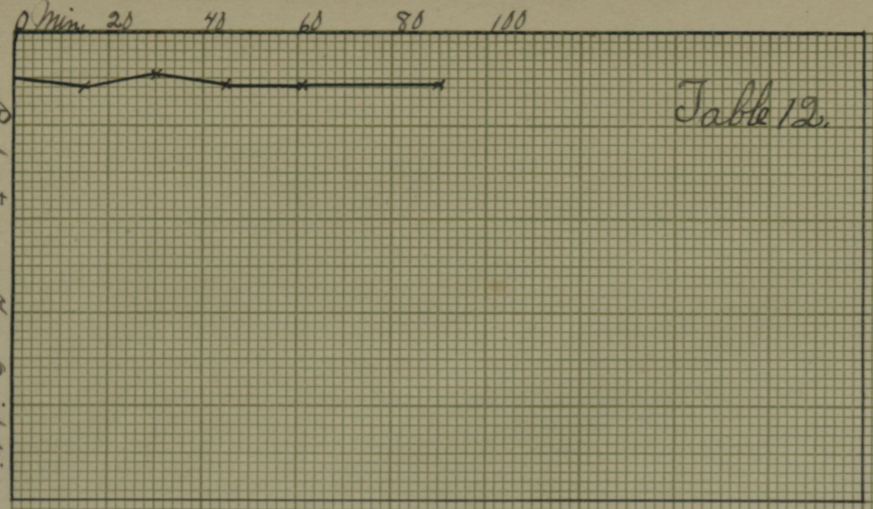
Time	cc oxidized	%
60	.87	23.9
90	.96	26.3
120	.99	27.2
180	.96	26.3
210	.91	25.0
225	.90	24.7

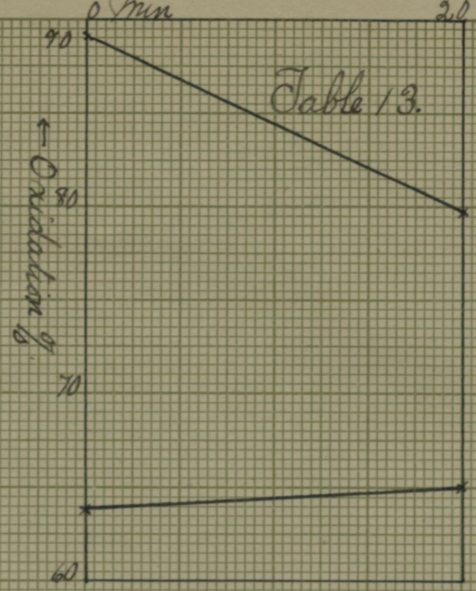
(b) Reduction.

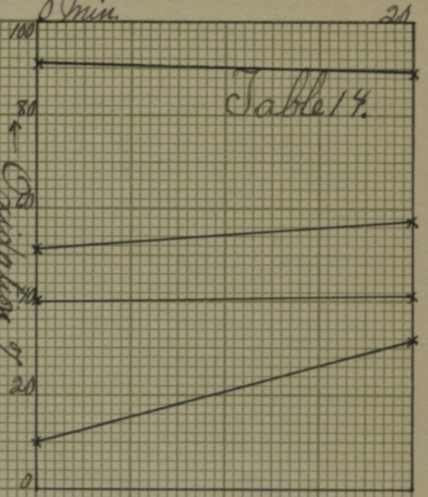
Time	cc reduced	%
60	.36	9.9
90	.385	10.5
120	.48	13.2
180	.475	13.0
210	.465	12.7
285	.48	13.2

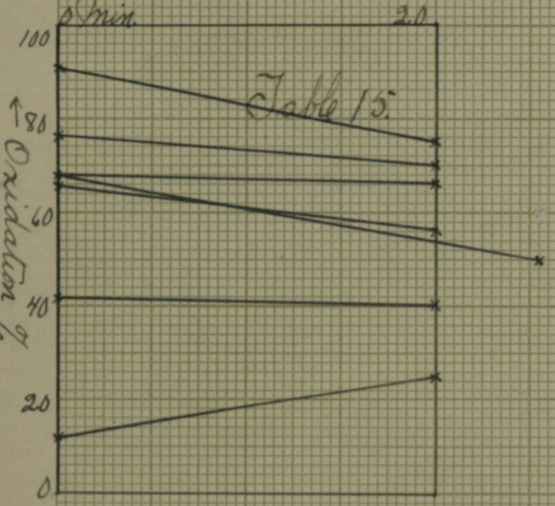
The above shows an oxidation of as much perhaps more than in Table 9. The reduction is greater.

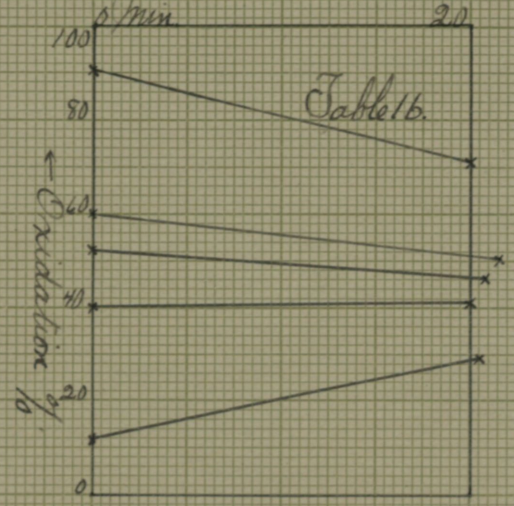
To facilitate the work still further a change was now made from a solution containing 100% ferric iron or 100% ferrous iron to one containing a mixture of the two. The principal idea in this was to determine more accurately the point of equilibrium. Since but one set of runs was made the table does not show a division into (A) Oxidation, and (B) Reduction as before.











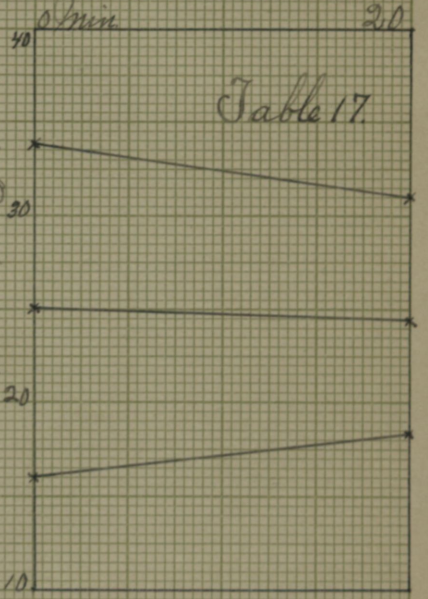


Table 11.

Rotating electrode: Pt gauze. Total volume 175 cc . No acid added. Solution made up to contain 90% Fe^{++} and 10% Fe^{+++} .

Time	Temp	$KMnO_4$ used	% Fe^{+++} at end.
0	-	3.64	10.0
15	37.0	3.28	9.8
30	38.0	3.21	11.8
60	40.0	3.09	15.2

As might be expected the percent of Fe^{+++} rises rapidly, or in other words the solution has been oxidized.

Changing now to the other side of the field:

Table 12.

10% Fe^{++} and 90% Fe^{+++}

Time	Temp	$KMnO_4$ used	%Fe^{++} at end.
15	39.0	.405	88.9
30	40.0	.35	90.4
45	41.0	.42	88.5
61	41.5	.435	88.1
75	42.0	.425	88.4
90	42.0	.43	88.2

The tendency toward equilibrium continues. The reduction does not seem to be as rapid as the oxidation. At this point work was discontinued for a time. Upon taking it up again, new solutions were made up. c.p. $FeSO_4$ was used instead of the reduced $Fe_2(SO_4)_3$. Solutions were restandardized, and burets recalibrated and as far as possible, after a consideration of the previous work, everything done to favor a most careful determination of the point of equilibrium, since the evidence brought out indicated its existence. The effect upon equilibrium etc. of acid did not warrant futher investigation but we wish to mention them

again when summarizing the results.
Temperature and Equilibrium.

Table 13.

Fe^{+++} and Fe^{++} mixed. Results expresses as % Fe^{+++} the remainder being always the % Fe^{++}. Current : 1.5 amp. Rotating electrode: Pt gauze, submerged area, 7979.6 sq mm. Stationary electrode: Pt wire, area 12.6 sq mm. Total volume 225 cc. .348 g Fe to 225 cc. Time: 20 min. (Temp. av. 2.8°) Percent Fe^{+++} at beginning and end based on $KMNO_4$ equivalent. 10 cc H_2SO_4 added.

Temp	% Fe^{+++} Beginning.	$KMNO_4$ used	% Fe^{+++} atend
4.6	89.17	5.65	79.69
1.0	63.85	10.53	65.06

The graphs representing the changes are taken only in the region under investigation: This average temperature of 2.8° is taken first as being the lowest convenient to use. By projecting the lines to the right to intersection, an approximate determination of the point of equilibrium is made. In this case it is 66.7% Fe^{+++} Following the same general plan a number of runs were made at a temperature a few degrees higher:

Table 14.

Av. temp. 5.2°

Temp.	%Fe^{+++} beginning	$KMNO_4$ used.	%Fe^{+++} at end.
8.5	40.60	18.36	41.47
8.3	10.52	19.67	31.92
3.8	90.35	3.54	89.27
0.0	51.80	13.85	57.50

Projecting to intersection equilibrium is found to be approximately 69.36 %Fe^{+++} . It is interesting to note that this elevation of equilibrium corresponds to that produced by the addition of H_2SO_4 but the change is much more rapid and definite.

Table 15.

Av . Temp. 36.5°. Time given in the table.

Time	Temp	%Fe+++ beginning.	$KMnO_4$	%Fe+++ at end
20	34.0	76.2	10.72	65.95
31	34.5	67.1	16.85	51.35
20	37.0	11.75	21.75	25.08
20	36.5	90.95	9.35	74.96
20	39.6	65.38	14.75	56.72
20	37.1	42.01	18.30	40.78

By projecting as before equilibrium appears at 44.68% Fe+++ .

Table 16.

Av. Temp 64.5°. Time given in table. Solution heated by large current (9.5 amp.) through it.

Time	Temp	%Fe+++ beginning	$KMnO_4$	%Fe+++ at end.
21.30 sec.	65.2	52.80	17.53	46.38
21	65.3	11.81	20.40	29.49
20	64.0	90.90	10.59	71.59
20	65.2	40.00	18.47	41.11

Equilibrium at 43.10%Fe+++ . Equilibrium continues to fall with rising temperature.

Table 17:

Av. temp. 90.2° Time 20 min.

Temp	%Fe+++ beginning.	$KMnO_4$	%Fe+++ at end.
90.3	33.86	21.13	31.05
90.1	16.07	24.22	18.41
90.2	25.07	22.63	24.65

Equilibrium 24.27% Fe+++ .

The above range of temperatures being the greatest obtainable with solutions in water the results are represented in Table 18.

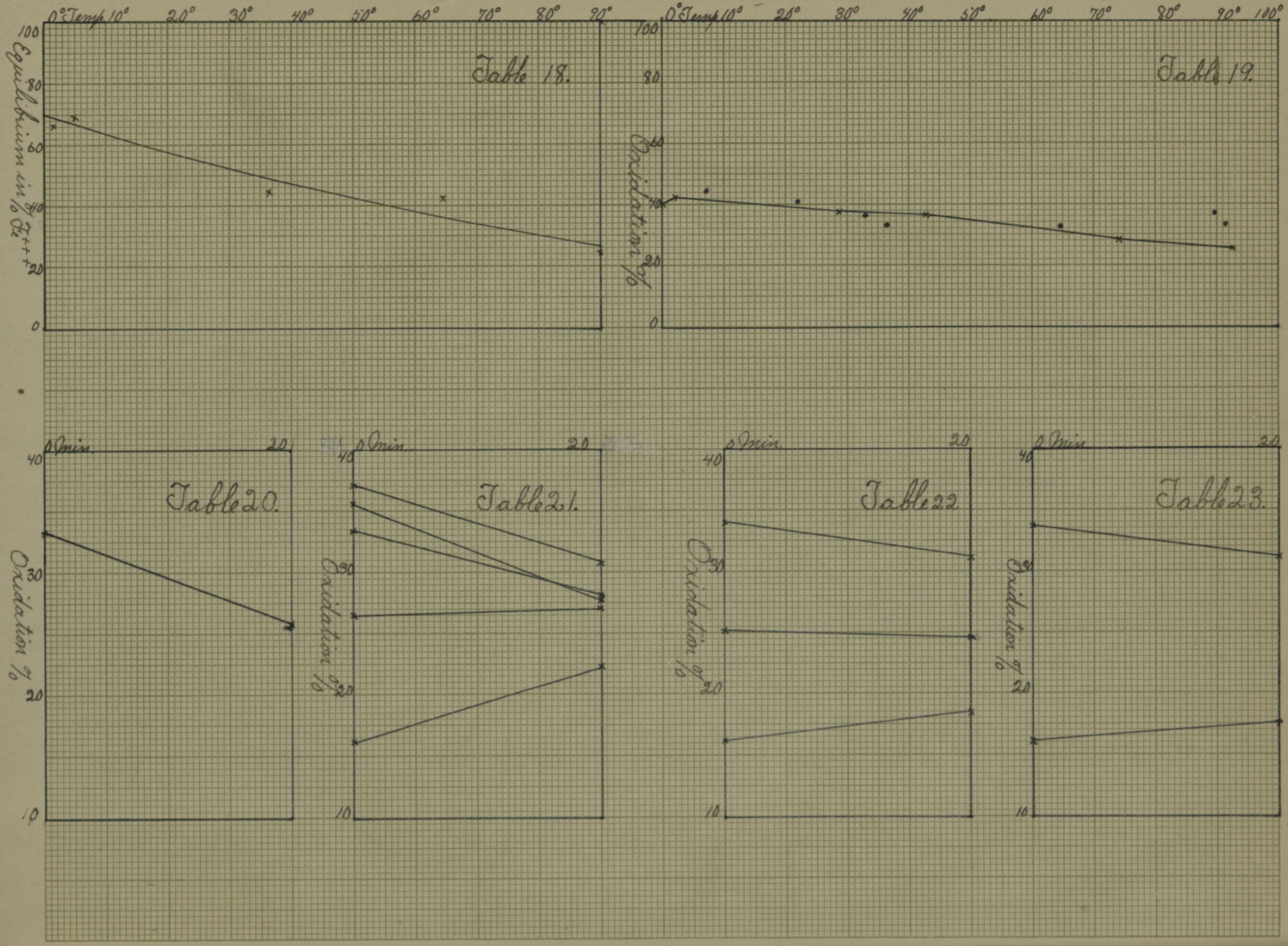


Table 18.
Equilibrium in % Fe+++
0° Temp. 10° 20° 30° 40° 50° 60° 70° 80° 90°
100
80
60
40
20
0
Table 19.
Oxidation %
0° Temp. 10° 20° 30° 40° 50° 60° 70° 80° 90° 100°
100
80
60
40
20
0
Table 20.
Oxidation %
0 Min. 20
40
30
20
10
Table 21.
Oxidation %
0 Min. 20
40
30
20
10
Table 22.
Oxidation %
0 Min. 20
40
30
20
10
Table 23.
Oxidation %
0 Min. 20
40
30
20
10

Table 18. A Summary of Temperature and Equilibrium.

Equilibrium determined by projection and intersection of straight line graphs.

Table	Ac. Temp.	Equilibrium in %Fe^{+++}
13	2.8°	66.7
14	5.2	69.36
15	36.5	44.68
16	64.5	42.10
17	90.2	24.27

A consideration of the equilibrium points plotted shows one first of all the fall of equilibrium with the rise in temperature and also that this fall is not represented by a straight line but by one that is convex downward, perhaps part of a hyperbola.

To afford a study of the above in a little different way a number of runs were made each beginning with 40% Fe^{+++} and 60% Fe^{++} giving the following results:

Table 19.

60 cycle alternating current (connected by straight lines on the graph)

Temp	Final % Fe^{+++}
2.2	42.55
28.5	37.86
42.8	36.12
74.3	28.69
92.8	25.54

The tendency toward high equilibrium for low temperature is greatly modified, the beginning % Fe^{+++} being 40. The whole curve is depressed toward the 0% Fe^{+++} line.

Employing the frequency changing apparatus, mentioned above with the

apparatus and to be used later, the solution was subjected to a frequency of about one third the above.

Table 19.

Proportions at the start: 40% Fe^{+++} and 60% Fe^{+++} .

Frequency: 23.02 cycles (Single dots on the graph.)

Temp.	Final % Fe^{+++}
3.4	44.38
7.3	44.06
22.2	40.40
33.3	35.08
36.3	32.97
64.7	32.94
89.8	37.62
91.5	33.74

The tendency toward equilibrium at a low % Fe^{+++} for high temperatures is not so well defined as with the 60 cycle current but at the lower temperatures a close relationship is shown.

Frequency and Equilibrium; By means of the variable frequency apparatus before mentioned currents of different frequencies were passed through the solution. The most important point here, perhaps is the possibility of verifying the assumption: that if a solution containing a limited amount of Fe^{+++} can be wholly reduced to Fe^{++} in eight minutes with a direct current and from all Fe^{++} to all Fe^{+++} in about the same time, then an alternating current of a frequency of one cycle or two reversals in sixteen minutes would cause the solution of Fe^{+++} to be wholly reduced and again wholly osidized in one cycle, or brought to equilibrium.

The lowest practicable frequency of the changing apparatus being about ten, results are given in;

Table 20 Time: 20 min.

Temp.	Cycles per sec.	%Fe^{+++} beginning	%Fe^{+++} at end	% change
91.4	10.05	33.30	25.93	83.90

The high temperature of 90° was selected because of the increased rate of reaction. By a consideration of the results in the temperature equilibrium trials as given above, 24.52% Fe^{+++} was taken as the nearest to point of equilibrium for 90°. Selecting now a convenient % of Fe^{+++} not too close to equilibrium, say, 33.0% Fe^{+++} then the change from 33.0% Fe^{+++} toward 24.52% Fe^{+++} represents the effect of the slowly alternating current in the given time, 20 min. It was found somewhat diffecult to make up a solution of exactly 33.0% Fe^{+++}, and 67.0% Fe^{++}, so the nearest % was taken from the table and interpolated back both for the beginning Fe^{+++} and the end Fe^{+++}. In Table 20. 33.30 Fe^{+++} beginning became 33.00 Fe^{+++} and 25.93 % Fe^{+++} became 25.63%.

Table 21.

Av. cycles: 23.5, Av. temp. 90.4, Equilibrium 26.27% Fe^{+++}

Temp.	Cycles	% Fe^{+++} beginning	% Fe^{+++} at end	% change
90.4	23.3	37.28	30.80	
90.1	23.3	35.71	27.83	
90.4	23.8	33.96	28.06	63.00
90.7	23.1	16.36	22.51	
90.3	23.9	26.54	27.38	

As will be noticed the slope of the curve beginning at 33.% Fe^{+++} is considerably less in Table 21 than in Table 20. The most simple explanation of this change may be based upon the theory of Wm. C. Arsem[1] in which he states: If a potential greater than the value of the electrode single potential be applied the negative ions give up their electrons which pass out on the anode wire and negative Cl ions become positive ions. The positive ions move away from the anode and combine with the ne-

1. Jour. Am. Chem. Soc. 36, 1671 (1914) Arsem.

gative Cl ions to form gaseous Cl_2. The electrode single potential is equal to the algebraic sums of the potentials represented by the attraction of the electrode material for the electrons, and the force necessary to remove an electron from a negative ion at the anode, or to add an electron to a positive ion at the cathode.

The potential difference being usually two volts, measured with a voltmeter, between the electrodes, it was evidently greater than the potential necessary to supply to or remove from the ions electric charges. If, now, a current be flowing, or better perhaps, one electrode is charged positively and the other negatively, for some considerable time a large number of ions lying near the electrode must be affected before they are swept away by the stirring. On the other hand if the period is shortened, as it is in changing from an average of 10.05 cycles to an average of 23.50 cycles, then some of the ions will not have been swept away from the region near the electrodes and will regain equivalent charges upon the reversal of the current and the consequent change of sign of the electrodes. The effect upon the iron ions which is relatively permanent and which is measured by titration at the end of the run is more quickly brought about by currents of the lower frequencies than by those whose frequencies are high. Table showing the effect at higher frequencies follow:

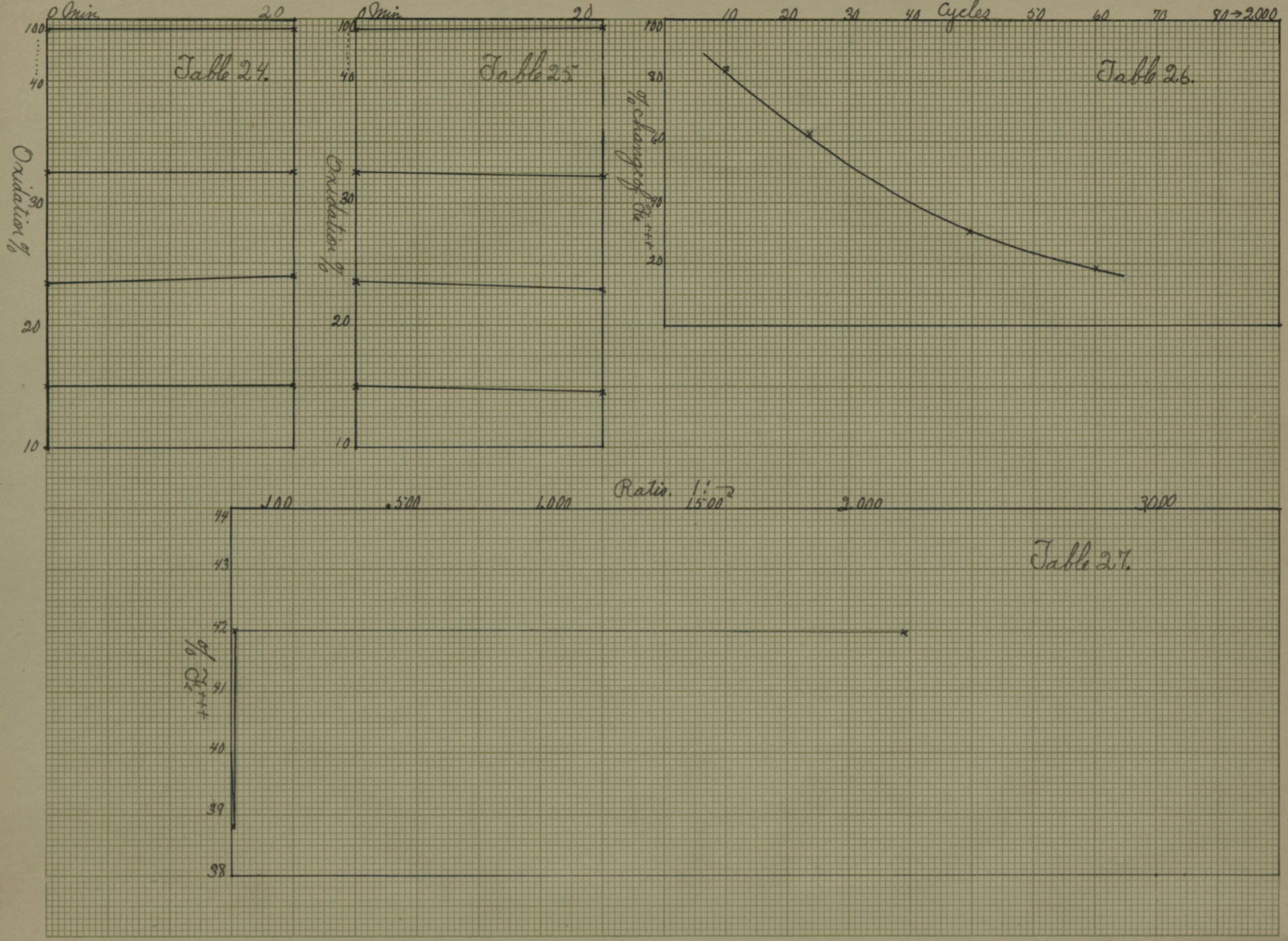
Table.22. Av. temp; 90.2, Av. Cycles:59.5 Equilibrium 24.27

Temp	Cycles	% Fe^{+++} beginning	%Fe^{+++} at end	% change
90.3	58.1	33.86	31.05	30.60
90.1	58.9	16.07	18.41	
90.2	61.4	25.07	24.65	

Table 23.

Av. Temp: 91.2°, Av. cycles:80.1, Equilibrium:27.61%Fe^{+++}

Temp	Cycles	%Fe^{+++} beginning	%Fe^{+++} end	% change
91.6	77.5	33.79	32.10	18.23
90.8	83.3	15.99	17.57	



As before stated the rate of change is based upon the change of the solution nearest 33.00% Fe at the beginning for this reason the percents of change of the other mixtures do not appear upon the tables. The other runs afford a check upon the point of equilibrium.

The frequency changing apparatus did not operate well for speeds greater than the 2400 revolutions per minute necessary to produce 80 cycles per second. The remainder of the runs were made with the Siemens, Schuckert high frequency generator.

Table 24.

Cycles: approximately 750 (The lowest speed of the generator).

Temp	%Fe^{+++} beginning	% Fe^{+++} at end	% change
91.3	32.53	32.74	No certain
89.4	15.06	15.33	change
91.1	23.50	24.04	
90.8	99.36	99.49	

It will be noticed that for 32.53, 15.06 and 23.50% there is almost a uniform tendency upward. This is very probably due to the difficulty in applying the proper oxidation correction. The run at 99.36% was made with the expectation that if there should be any change it would show itself in this region, and it is true that the graph does not rise quite so much as those at the lower percents.

Table 25. Cycles 2000 (Highest of high frequency app.) Av. Temp:91.2°

Temp	%Fe^{+++} beginning	%Fe^{+++} at end.	% change
92.9	32.62	32.34	0
90.6	15.14	14.61	
89.8	23.56	23.16	
91.6	99.36	99.47	

No recognizable effect appears at 99.36% Fe^{+++}

The following table is self explanatory being a summary of the above.

Table 26.

Cycles and Rate of Change (% reduction of 33.00% Fe^{+++} toward equilibrium in the run of 20 min.)

Cycles	% change
10.05	83.90
23.50	63.00
59.50	30.60
80.10	18.23
750.00	?
2000.	0

This curve is also apparently a hyperbola similar to that of Table 18 and having rectangular asymptotes.

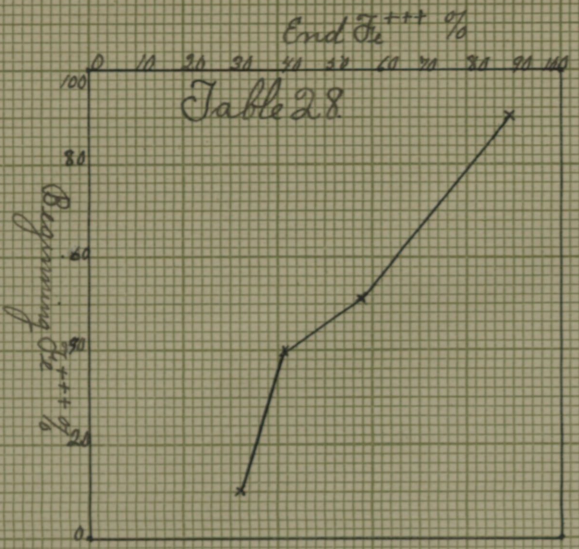
For differing relative electrode area the following results were obtained:

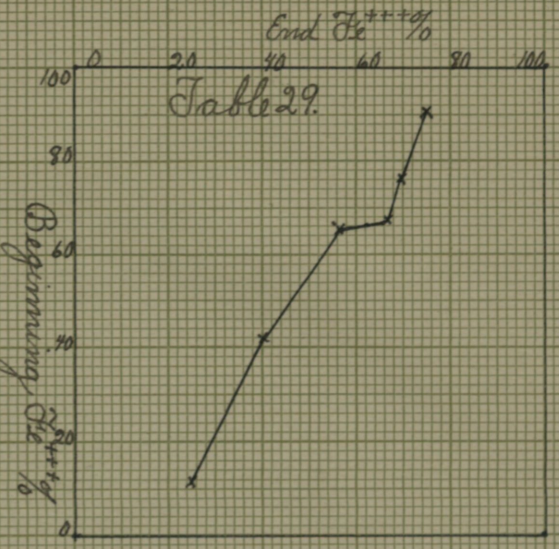
Table 27 Cycles:60 Av. Temp. 34.8

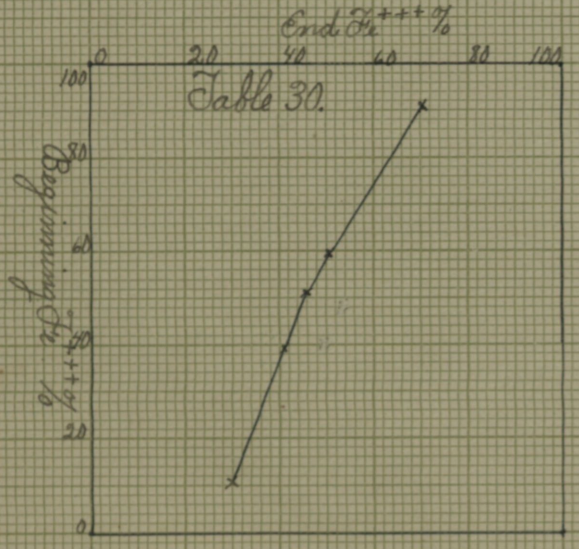
Temp	Rotating Electrode.	Stationary Electrode.	Ratio Rot: Sta. 1:x.	%Fe+++ beginning	%Fe+++ end	*Fe end
37.1	Pt gauze, 7979.6 sq. mm.	Pt wire 12.6 sq. mm	1:.0015	42.01	40.78	38.77
33.3	" " "	" " 72.9 " "	1:.009	40.65	42.77	42.12
33.9	" " "	† " gauze 17422.7" "	1:2.185	40.67	42.61	41.94

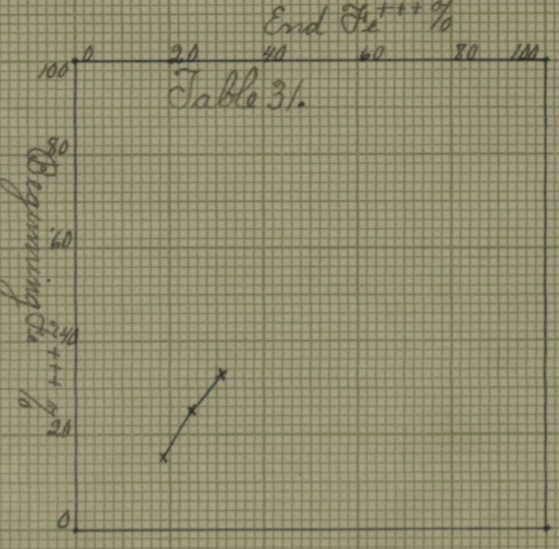
*Beginning Fe^{+++} reduced to 40.00% and end Fe^{+++} correspondingly changed for comparison. † Stationary gauze found filled with bubbles of gas at end of run.

By referring to Table 18 it will be seen that for a temperature of 34.8° equilibrium is very close to 50% Fe^{+++}. It may be expected, then, that when starting with 40 or 42% Fe^{+++} the solution will begin oxidizing up to 50% Fe^{+++}, or equilibrium. It was assumed at the time the runs were made, before the data was gone over as carefully as it was later, that the point of equilibrium for this temperature was approximately 42.% Fe^{+++} and hence if there was oxidation or reduction it would be due to the change in the relative sizes of the electrodes. The changes which did take place are entirely out of proportion to the









change in electrode area for the area of the gauze in the third run was nearly 1500 times as much as that of the wire used in the first run and the difference between the final percents of Fe^{+++} in these two runs is only about 3.2%. It would seem to be pretty evident, from these results, that equilibrium is not dependent upon the relative electrode area.

Before bringing out the final conclusions a few miscellaneous points should be mentioned. The following are tables in which the beginning percent Fe^{+++} has been plotted as ordinate and end percent Fe^{+++} as abcissa at temperatures ranging from 0° to 95°.

Table 28.

Temp. 0° to 10° Values found in tables already given.

Table 29.

Same as Table 28 except temp. 30° - 40°.

Table 30.

Same as Table 28 except temp. 60°- 70°.

Table 31.

Same as Table 28 except temp. 85°- 95°.

As has already been shown for high concentration of Fe^{+++} and low temperature, equilibrium is at a point corresponding to this high concentration and the beginning percent Fe^{+++} remains nearly the same to the end. For low concentrations of Fe^{+++} at the low temperature there is a change toward a higher concentration and hence in Table 28 where the temperature was 0°- 10° Fe^{+++} starts at 10% and the ends at nearly 32%. If there had been no progress toward equilibrium the graph would be a diagonal from "0% beginning Fe^{+++}" to "100% ending Fe^{+++}." As it is the graph has swung away from the "Beginning Fe^{+++} side, turning about the point" 100% Fe^{+++} end" as an axis, or center. In tables 29 and 30 the axis or center of turning has moved away from the "Beginning Fe^{+++} End"

until in Table 30 it occupies a point past midway on the diagonal. Both ends of the graph have moved from the diagonal and in an anti-clockwise direction. In Table 31 eqiilibrium is not far from 0% Fe^{+++} Beginning, and the upper and only of the graph swings away from the diagonal.

As before stated it has been shown by Allen that a direct current, with suitable electrodes, will reduce a solution of ferric iron, where the concentration is not too high, in about eight minutes. Nothing definite being known of the opposite effect, or where the rotating electrode was made anode and the stationary wire electrode made cathode in a solution of ferrous iron, the following run was made:

Table 32.

Direct current. Cathode: stationary Pt wire, area 12.6 sq mm. Anode: rotation Pt gauze, Area 7979.6 sq mm. 1.5 amp.

Time	Temp	cc Fe^{++} beginning	$KMnO_4$	%oxidized
30	35.3	49.97	.01	99.96

A strong end point was gotten when the measured amount (.01) of $KMnO_4$ was added in the titration. It is probable that oxidation was more nearly complete than the 99.96% obtained by the calculation. It was noticed that the solution had changed to the peculiar greenish color characteristic of ferric iron before ten minutes had elapsed. This indicated that complete oxidation had been accomplished almost if not as quickly as complete reduction was brought about by a current flowing in the opposite direction. These results need not be taken as opposing in any way the possibility of establishing equilibrium with a rapidly alternating current for the use of the rotating gauze is equivalent to making one electrode infinitely larger than the other giving no opportunity for the established equilibrium so easily shown by the alternating current.

Conclusion: An examination of the above results leads to the following general conclusions:

1. When acted upon by an alternating electric current, iron in solution, tends to establish an equilibrium between the percents of ferric and ferrous iron present.

2. The point of equilibrium is affected by temperature, being, when expressed in terms of ferric iron, high at low temperatures and low at high temperatures.

3. Frequency influences the rate at which the solution comes to equilibrium. With low frequencies (as low as 10 per sec. at least) equilibrium is reached quickly, but very slowly reached with high frequencies.

4. The relative size of the electrodes has little or no effect upon the point of equilibrium.

5. High acidity causes the solution to come to equilibrium more slowly and produces a tendency toward oxidation, or an elevation of the point of equilibrium.

6. A solution of iron containing approximately .35 g in the ferrous state may be completely oxidized in 30 min. using a direct current and suitable electrodes.

7. An alternating current of 10 cycles per sec. at 90° C will produce a movement of 80% toward equilibrium in 20 min. For complete equilibrium 2 to 3 hours are required.

As a practical method for determining equilibrium between "ic" and "ous" ions of all elements known to exist in these states it seems well adapted.

Acknowledgement is due to the Manual Training department of Argentine High School in charge of M.S.Perrault for the rotating electrode machine used in the latter two thirds of the work and for assistance in preparing the drawing and blueprint of the frequency changing apparatus.